Name ___________________________**Chem 163 Section**: ______ **Team Number:** ______

ALE 25. Cell Potential and ΔG_{rxn} for a Voltaic Cell

(Reference: 21.4 Silberberg *5th edition*)

How much work can be done by a battery of a given voltage?

The Model

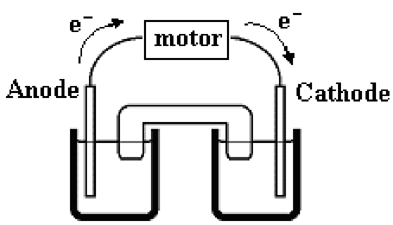
As we learned in the previous ALE, the potential (measured in Volts) of an electrochemical cell operating at standard state is simply the difference between the standard-state reduction potentials of the two electrodes that comprise the cell:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} \quad \text{or} \quad E^o_{cell} = E^o_{red} + E^o_{ox}$$

The **volt** is defined as: $1\,\text{V} = \dfrac{1\,\text{J}}{1\,\text{C}}$

Electrical charge is measured in Coulombs with the **charge of one electron = 1.60218 x 10^{-19}C.** Hence **1 C equals the charge of electrons 6.2415 x 10^{18}**.

Suppose a voltaic cell is constructed such that the cell's potential were 1 V. Further suppose an electric motor is placed between the two half-cells. Based on the definition of the volt, if one **coulomb** of charge passes from one electrode to the other in which the cell potential is **one volt**, then the electrons can do **one joule of work**.



Key Questions

1. Because chemists regularly use the unit of moles (1 mol = 6.0221 × 10^{23} particles), it is convenient to define the faraday (symbolized by $\mathcal{F}$) as the charge of one mole of electrons. The **Faraday** is *the charge in coulombs of one mole of electrons*. Use the information in the model, above to calculate the correct 5-digit number to fill in the following blank. *Show your work*.

$$1\,\mathcal{F} = \_\_\_\_\_\_\_\_\_\_ \left(\frac{\text{C}}{\text{mole}^-}\right)$$

2. Suppose there are two voltaic cells. Cell A operates at 1 V and cell B operates at 2 V. Which of the following is true if the same electrical motor is attached to the two cells? Circle the correct answer and *briefly explain your reasoning*.
   i. Cell A produces a greater amount of work per mol of electrons than cell B.
   ii. Cell B produces a greater amount of work per mol of electrons than cell A.
   iii. Both cell A and cell B produce the same amount of work per mol of electrons.

3. In the last ALE, we determined that the Al-H^+, the H_2-Ag^+, and the Al-Ag^+ cells have the following half-reactions:

Cell	Half-reactions	
Al-H^+	$Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-$ $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$	$n = 6$
H_2-Ag^+	$H_2(g) \rightarrow 2\ H^+(aq) + 2\ e^-$ $Ag^+(aq) + e^- \rightarrow Ag(s)$	$n = 2$
Al-Ag^+	$Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-$ $Ag^+(aq)\ e^- \rightarrow Ag(s)$	$n = 3$

What does the value of n represent?

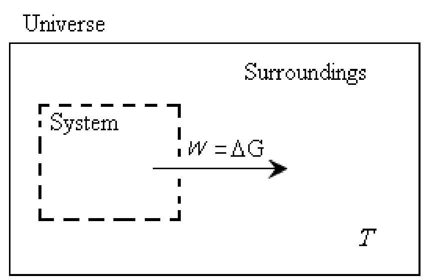
4. Per mole of the anode (*e.g.*, solid aluminum) that is "consumed" (i.e. oxidized) when a voltaic cell is in operation, is the amount of work that the electrons can do as they pass through a motor on their way to the cathode *directly dependent*, or *inversely dependent*, or *independent* on the number of electrons that pass through the motor? (Circle your response.)

5. The electrical work (***w***, in J/mol) done *by* the reactants of the cell reaction that occurs spontaneously in a voltaic cell with potential $\boldsymbol{E}_{\mathbf{cell}}$ is given by eqn **1**. Fill in the blank with the appropriate symbol. *Use dimensional analysis to show how you arrived at your answer*. *Hint*: The variable, ***n***, the number of electrons transferred in the redox reaction, is unitless. Consider the units of ***w*** and $\boldsymbol{E}_{\mathbf{cell}}$, keeping in mind the definition of the volt, J/C.)

$$|w| = n \_\_\_\_ E_{\text{cell}} \qquad (\mathbf{1})$$

6. a. Does the figure on the right suggest that…
   i. *work is being done by the system* or that
   ii. *work is being done on the system*?
   (Circle your choice.)

   b. Is $\Delta G < 0$ or $\Delta G > 0$ as shown?
   Circle your choice and briefly explain your reasoning.



7. When we recognize that the change in Gibbs free energy for a cell reaction is the maximum amount of electrical work that a voltaic cell can do per mole of reactants, we develop eqn **2**.

$$\Delta G_{rxn} = -n\mathcal{F}E_{cell} \qquad (2)$$

a. A spontaneous cell reaction has: (Circle your response.)

i. $\Delta G_{rxn} < 0$ and $E_{cell} < 0$ iii. $\Delta G_{rxn} > 0$ and $E_{cell} < 0$

ii. $\Delta G_{rxn} < 0$ and $E_{cell} > 0$ iv. $\Delta G_{rxn} > 0$ and $E_{cell} > 0$

b. A nonspontaneous cell reaction has: (Circle your response.)

i. $\Delta G_{rxn} < 0$ and $E_{cell} < 0$ iii. $\Delta G_{rxn} > 0$ and $E_{cell} < 0$

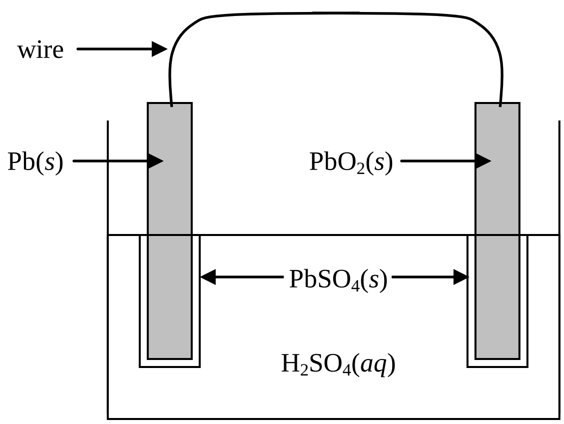
ii. $\Delta G_{rxn} < 0$ and $E_{cell} > 0$ iv. $\Delta G_{rxn} > 0$ and $E_{cell} > 0$

Exercises

The overall reaction that occurs in the voltaic cell known as the "lead storage battery" is shown as eqn **3**.

$$\mathbf{Pb}(s) + \mathbf{PbO_2}(s) + \mathbf{2\ H^+} + \mathbf{2\ HSO_4^{1-}} \rightarrow \mathbf{2\ PbSO_4}(s) + \mathbf{2\ H_2O}(l) \qquad (3)$$

A schematic drawing of a voltaic cell in a **lead storage battery** is shown below.



8. What are the oxidation and reduction half-reactions that take place in the lead storage battery? (*Hint*: Use the table of standard reduction potentials in your textbook. Look for half reactions that involve Pb, PbO_2, and $PbSO_4$.) What are E^o_{ox}, E^o_{red}, and E^o_{cell} at 25 °C? (By the way, when six of these voltaic cells are connected "in series", the resultant battery has a potential of ~12 V.)

Half reaction at anode: ____ E^o_{ox} = ______v

Half reaction at cathode: ____ E^o_{red} = ______v

E^o_{cell} =

9. Why is a salt bridge unnecessary in the lead storage battery?

10. Write the cell diagram for the lead storage battery. (Identify the substance that serves as the anode. The cell diagram should go from the anode to the cathode, identifying one phase at a time.)

11. Use *n* and E^o_{cell} for the reaction that occurs in the lead storage battery to determine ΔG^o_{rxn} (in kJ/mol) for the reaction that occurs within one cell of a lead storage battery.

12. ΔG^o_f for $PbO_2(s)$ is -217.4 kJ/mol at 25 °C. Use this, eqn **3**, the tabulated thermodynamic data in Appendix B of your textbook, and Hess's Law to calculate ΔG^o_f for $PbSO_4(s)$ at 25 °C. For simplicity, in this problem, consider 1 *M* $H_2SO_4(aq)$ to be 100% dissociated into 2 $H^+(aq)$ and $SO_4^{2-}(aq)$:

$$Pb(s) + PbO_2(s) + 4\,H^+ + 2\,SO_4^{2-} \rightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$$